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TITLE: HIGH DENSITY BORON NITRIDE MATRIX
COMPOSITES

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HIGH DENSITY BORON NITRIDE MATRIX COMPOSITES

FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

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BACKGROUND

10 Materials which do not deteriorate mechanically and continue to function
in extreme conditions of temperature, friction and wear, are desirable and
necessary in a wide range of modern applications. The materials of aircraft brakes
experience some of the harshest service conditions seen in any application. The
material experiences high friction and temperatures while the aircraft is taxiing
and landing. In addition, all aircraft brake materials are required to withstand the
15 extreme conditions of rejected take-off (RTO) trials.

One class of materials used for aircraft brakes is composites of carbon
fibers reinforcing a carbon matrix (C/C composites). These materials are
described in J. Economy, H. Jung and T. Gogeva, Carbon, Vol. 30, No. 1, pp 81-
85 (1991).

20 C/C composites are considerably stronger and lighter than steel. Such
materials increase in strength with increasing heat treatment and resist thermal
shock caused by rapid temperature changes. However, they suffer from a number
of drawbacks including poor oxidation resistance, highly variable wear rate and
coefficient of friction, and costly manufacturing. The lack of high temperature
25 stability requires an expensive supplementary processing step to coat the non-
frictional surfaces with an oxidation barrier. In addition, fabrication is very time
consuming (1-2 months) due to the long periods required for chemical vapor
infiltration of the carbon matrix. Thus, the fabrication is a slow, expensive process.
The carbon matrix is usually introduced among the carbon fibers by liquid

impregnation and charring of organic materials. In some applications, chemical vapor deposition is used as a final step in processing. The steps in the processes are repetitive and can take months to complete. These materials are also only moderately oxidation resistant, thus requiring the addition of an expensive
5 oxidation barrier coating to the non-frictional surfaces. Furthermore, they have a highly variable coefficient of friction, especially in the presence of water, which causes variable brake feel to pilots (nicknamed "morning sickness").

Carbon fibers reinforcing a boron nitride matrix (C/BN composites) have the potential to overcome some of the shortcomings of C/C composites. These
10 materials are prepared by first polymerizing borazine ($B_3N_3H_6$), to yield an oligomer of appropriate viscosity that is used as a boron nitride precursor for impregnating the carbon fibers. The impregnated fibers are then heated under pressure, yielding a solid boron nitride matrix reinforced by the carbon fibers. The preparation time for such composites requires days, as opposed to the months
15 needed for C/C composites, with concomitant cost savings (U.S. Pat. No. 5,399,377). However, due to low density, the resulting C/BN composites do not have acceptable heat capacity and thermal conductivity values to substitute for C/C composites in aircraft brakes. The preparation typically yields a composite with a density in the range of 1.38 g/cc to 1.43 g/cc, and with multiple
20 impregnations (up to six) the density increases up to 1.61 g/cc. Additional impregnations do not appear to effectively increase the density of the composites.

Consequently, C/BN composites have higher oxidation resistance than C/C composites, but do not have the desired density of about 1.8 g/cc which is expected to be necessary for the materials to have the heat capacity and thermal
25 conductivity needed for good braking.

The performance of C/C composites may also be improved by the addition of a boron nitride matrix, yielding carbon fiber composite materials with a boron nitride layer, or C/C/BN composites. These materials are prepared by immersing lower density C/C composites in borazine oligomers and subjecting the system to the same procedure used for C/BN composites (U.S. Patent No. 5,399,377). The
30 boron nitride coating renders the product more oxidation resistant than C/C

composites. Nevertheless, the density of C/C/BN composites is still below the level required for aircraft brakes applications, and their wear rate is too high once the thin BN coating is worn away (Brian Fabio, M.S. Thesis, The University of Illinois at Urbana-Champaign).

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SUMMARY

In a first aspect, the present invention is a method of manufacturing a composite material comprising forming a mixture comprising a plurality of fibers and a borazine oligomer; subjecting the mixture to a first heating, for 12 hours to 56 hours; and subjecting the mixture to a second heating. The temperature of the first heating is 60 °C to 80 °C, and the pressure during the first heating is at least 0.5 MPa, the temperature of the second heating is at most 400 °C, and the greatest pressure of the second heating is at least 15 MPa.

In a second aspect, the present invention is a composite material comprising carbon fibers in a boron nitride matrix. The composite material has a density of at least 1.62 g/cc.

In a third aspect, the present invention is a composite material comprising carbon fibers in a boron nitride matrix. The composite material has a wear rate of at most 0.4 mg/m at an energy level of 100 kJ/kg to 1100 kJ/kg, and a coefficient of friction of at least 0.22 at an energy level of 100 kJ/kg to 1200 kJ/kg.

In a fourth aspect, the present invention is a method of manufacturing a composite material comprising boron nitride, comprising forming a mixture comprising a preform and a borazine oligomer; subjecting the mixture to a first heating, for 12 hours to 56 hours; and subjecting the mixture to a second heating. The temperature of the first heating is 60 °C to 80 °C, and the pressure of the first heating is at least 0.5 MPa, and the temperature of the second heating is at most 400 °C, and the greatest pressure of the second heating is at least 15 MPa.

In a fifth aspect, the present invention is a composite material comprising a 3D needled carbon fiber preform impregnated with boron nitride having a density of at least 1.63 g/cc.

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In a sixth aspect, the present invention is a composite material, comprising CVI-infiltrated carbon fiber preform impregnated with boron nitride having a density of at least 1.62 g/ cc.

In a seventh aspect, the present invention is a composite material comprising a 3D needled carbon fiber preform impregnated with boron nitride having a wear rate of at most 0.05 mg/m at an energy level of 100 kJ/kg to 1000 kJ/kg, and a coefficient of friction of at least 0.12 at an energy level of 100 kJ/kg to 900 kJ/kg.

10 BRIEF DESCRIPTION OF FIGURES

Figure 1 illustrates a thermogravimetric analysis (TGA) experiment performed on a 1:1 mixture of carbon fibers and borazine.

Figure 2 is the X-ray diffraction scan of the C/BN composites of the invention, showing that the d-spacing of BN is 3.36 Å.

15 Figure 3 is a plot of the wear rate for traditional C/C composites, traditional C/C/BN composites, and the high density C/BN composites of the invention.

Figure 4 is a plot of the coefficient of friction (COF) for traditional C/C composites, traditional C/C/BN composites, and the high density C/BN composites of the invention.

20 Figure 5 is a plot of the wear rate at 160 psi for the high density C/BN material of the invention and for traditional lower density C/BN materials.

Figure 6 is a plot of the coefficient of friction (COF) at 160 psi for the high density C/BN material of the invention and for traditional, low density C/BN materials.

25 Figure 7 is the X-ray diffraction scan of the 3D C/C/BN composites of the invention, showing that the d-spacing of BN is 3.38 Å.

Figure 8 is a plot of the wear rate, at a pressure of 0.25 MPa, of traditional 3D C/C composites, the 3D C/BN composites of the invention, and of the 3D C/C/BN composites of the invention.

Figure 9 is a plot of the wear rate, at a pressure of 0.5 MPa, of traditional 3D C/C composites, the 3D C/BN composites of the invention, and of the 3D C/C/BN composites of the invention.

5 Figure 10 is a plot of the coefficient of friction (COF), at a pressure of 0.25 MPa, of traditional 3D C/C composites, the 3D C/BN composites of the invention, and of the 3D C/C/BN composites of the invention.

10 Figure 11 is a plot of the coefficient of friction (COF), at a pressure of 0.5 MPa, of traditional 3D C/C composites, the 3D C/BN composites of the invention, and of the 3D C/C/BN composites of the invention.

DETAILED DESCRIPTION

The present invention provides a new type of C/BN composites with densities averaging 1.75 g/cc, and methods for their fabrication. These C/BN composites were found to outperform C/C composites in testing, and their density renders them a viable substitute for C/C composites in applications of friction and wear. The invention is based on the discovery that higher density C/BN composites can be formed when carbon fibers impregnated with borazine oligomers are heated under a pressure exceeding 0.5 MPa, and the pressure is applied before the temperature reaches 400 °C.

20 These high density C/BN composites are prepared by first heating the borazine monomer in a pressure vessel, with occasional venting, at a temperature of 60 °C to 80 °C, more preferably 65 °C to 75 °C, and, most preferably, 68 °C to 72 °C. The borazine reacts with itself to yield oligomers while releasing hydrogen as a primary by-product, and the heating is applied until a viscosity of 500 cP to 2500 cP is attained, usually within 24 to 48 hours. The oligomers are used to 25 impregnate carbon fibers, and the resulting system is heated to 60 °C to 80 °C, more preferably 65 °C to 75 °C, and most preferably, 68 °C to 72 °C, under a pressure ranging from 0.5 to 8 MPa, more preferably 1 to 5 MPa, and most preferably 2.2 to 4.4 MPa, for preferably 12 to 48, hours to induce further oligomerization of the borazine without formation of voids.

The composite is then subject to increasing temperature and pressure under an inert atmosphere. The heating promotes further borazine polymerization while the pressure is controlled to achieve a high density product. The temperature is increased to 300 °C to 400 °C at a rate of 0.25 °C/min to 3 °C/min, more
5 preferably to 325 °C to 375 °C at a rate of 0.75 °C/min to 1.25 °C/min, yet more preferably to between 340 °C to 360 °C at a rate of 0.9 °C/min to 1.1 °C/min. The pressure is ramped to a final pressure of 14 MPa to 30 MPa, more preferably from 18 MPa to 26 MPa, and most preferably, 21 MPa to 23 MPa. The composite is then preferably held at the final temperature and pressure for an additional 10 to
10 30 hours, more preferably 16 to 24 hours.

The resulting composite is preferably heated at 5 °C/min to 15 °C/min to a final pyrolysis temperature of 1100 °C to 1500 °C, for 1 to 3 hours, and then cooled, more preferably heated at 10 °C/min to a final pyrolysis temperature of 1150 °C to 1250 °C, for about 2 hours. This process is optionally carried out two
15 or three times to maximize the density of the product.

The process described above was also applied to 3D needled carbon fiber preforms. The hydrogen and other by-products appear to easily escape from the preform, yielding a new type of high density 3D C/BN material with as little as a single impregnation. In addition, it was found that optimal wear properties were obtained when the 3D carbon preform was first subjected to carbon CVI to a density of ~1.3 g/cc and then impregnated with borazine oligomer and subjected to the process above, yielding a new higher density 3D C/C/BN material.
20

Objects of various shapes may be fabricated by using the materials of the invention in resin transfer molding processes (RTM). In RTM, a fiber preform, with the shape of the desired object, is loaded into a mold without the borazine. Alternatively, the preform may be bent into the desired shape by the walls of the mold. The mold is closed, and borazine or the borazine oligomer as described above is injected or transferred into the mold and impregnates the preform. The resulting system is then subjected to the same temperature and pressure treatment
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as described above, yielding objects with increased densities and complex shapes in faster processing times.

EXAMPLES

5 1) Thermogravimetric analysis of the C/BN composite production process

One possible explanation for the higher density of the materials of the invention may be that the pressure prevents the hydrogen evolving from the transformation of the borazine into boron nitride from forming bubbles that would lead to a porous, lower density structure. To investigate this possibility, a series of 10 thermogravimetric analysis (TGA) experiments were done using a 1:1 mixture of carbon fibers and borazine.

Figure 1 is a representative TGA showing that the majority of the hydrogen and other by-products evolved from the borazine below 150 °C. This indicated that applying pressure would be most effective below this temperature for two reasons: (1) after attaining 150°C the viscosity would become too high and the sample less compressible; (2) this is the region where most of the hydrogen by-product is being produced, a high pressure at this temperature could help prevent the introduction of pores into the matrix structure. In general, the system should be maintained under pressure at a temperature of at most 150 °C until about 80% of 15 20 the weight loss due to borazine polymerization has occurred. However, pressure during the higher temperature processing, 150 °C to about 350 °C, is still essential in order to keep the evolving hydrogen from creating porosity in the structure.

2) Preparation of high density C/BN composites

25 Borazine monomer was oligomerized in an inert atmosphere at 70 °C for 36 hours, until an oligomer of viscosity of 500 to 2500 cP was attained. In a dry box, chopped carbon fibers were placed into a two inch diameter mold and a measured amount of the borazine oligomer was added. Graphite foil was then placed on top of the sample (as a releasing agent) followed by a tightly fitting disk 30 of TEFLON® (DuPont, Wilmington, DE) to prevent potential leakage of borazine.

To provide extra mechanical support to the TEFLON® a precisely machined brass disk was placed on top of the TEFLON®. A steel plunger was then placed on top of the brass and the entire assembly transferred into a controlled atmosphere hot press. The mold and the sample were then heated to 70 °C and held isothermally for an additional 48 hours under pressure. Pressure was applied while the temperature was increased to 350 °C at a rate of 1 °C/min under dry nitrogen. The composite was then held at 350 °C for 20 hours under constant pressure.

Following this final oligomerization, the composite was removed from the mold and separated from the graphite foil. The composite was then placed in a mullite tube furnace which was backfilled with dry nitrogen. The furnace was ramped at 10 °C/min to a final pyrolysis temperature of 1200 °C, held for two hours, and then cooled. The processing schedule, shown in Table 1, describes the temperatures and the pressures applied. From a single impregnation bulk densities in the range of 1.3 to 1.55 g/cc were achieved using 40% V_f (fiber volume fraction) chopped pitch based carbon fibers. This process was carried out three times to maximize the density to approximately 1.75 g/cc.

Table 1

Temperature °C	Pressure (MPa)	Hold Time (hrs)
70	2.2	48 1 °C/min ramp
90	4.4	
110	13	
130	15	
150	22	
350	22	
1200	-	10 °C/min ramp, 2 hr hold

During the reimpregnations a similar temperature-pressure process was used with one additional step prior to hot pressing. This involved placing the composite in a steel pressure vessel and heating under vacuum for 30 minutes,

backfilling with nitrogen and then introducing enough borazine oligomer to
submerge the composite. The system was then held at 70 °C for 12 hours, with
occasional venting to reduce the partial pressure of hydrogen. This allowed for
better permeation of the composite and caused the borazine oligomer molecular
5 weight to increase while filling in the porous structure. As an example, one
composite exhibited an initial density of 1.46 g/cc and one, two and three
impregnations yielded increased densities of 1.62, 1.66 and 1.75 g/cc, respectively.

3) X-ray diffraction data of C/BN composites

10 The X-ray diffraction data depicted in Figure 2 shows that the interlayer, or
d-spacing, of the BN in the C/BN composites is 3.36 Å. It is known that hexagonal
BN with d-spacings below 3.38 Å display greatly increased resistance to
hydrolysis (C.G. Cofer and J. Economy, "Oxidative and hydrolytic stability of
boron nitride", Carbon, Vol. 33, No. 4, p. 389). The BN d-spacing is calculated
15 from the sharp peak labeled on the scan, appearing at 26.435°.

4) Wear rate testing of high density C/BN composites

Once the C/BN composites reached a density of approximately 1.75 g/cc,
friction and wear testing was performed on an inertial brake dynamometer. This is
20 the most important parameter since it determines the lifetime and safety of the
brake material. The resulting wear rate plotted versus energy level for previously
tested C/C, C/C/BN, and the new C/BN composites of the invention appear in
Figure 3. The shapes of the curves for the C/C and C/C/BN composites are similar,
though C/C/BN exhibits a wear rate lower than the C/C at all levels. C/BN
exhibits a wear rate significantly lower than the C/C in the two problematic
25 regions, namely low energy levels (taxi conditions) and high energy levels
(Rejected Takeoff). A significant amount of wear over the lifetime of a C/C
aircraft brake occurs during taxiing. In this region the C/BN displays a four-fold
decrease in wear-rate, implying the potential for a significant increase in the
30 number of landings between overhauls. At an energy level of approximately 600

5 kJ/kg the wear rate of the C/C material begins to increase. This increase in wear rate corresponds to the onset of oxidation of the carbon. In comparison, the C/BN does not display significant oxidation until much higher temperatures (900-1000 °C for short times), which would correspond to energy levels of approximately 1200 kJ/kg. Another advantage of this increased resistance to wear at high temperatures would be that the addition of an expensive oxidative barrier coating (as used with commercial C/C) would not be necessary.

10 5) Comparison with traditional C/BN materials.

15 The wear rate of the C/BN material of the invention is also markedly better than that of a traditional, lower density C/BN material produced according to the process of U.S. Patent No. 5,399,377. As illustrated in Figure 5, the wear rate of the C/BN of the invention is consistently below 0.5 mg/m, whereas the traditional C/BN material exhibited wear rates reaching above 2 mg/m.

20 15 6) Friction testing of high density C/BN composites

25 The average coefficient of friction (COF) is plotted versus energy levels in Figure 4. The resulting COF for the C/BN composites was found to be much less sensitive to energy, and therefore temperature, than C/C composites. Typically, the COF for C/C composites varies widely from 0.1 to 0.5 depending on the temperature. In contrast, the COF for the C/BN composites varied only from 0.22 to 0.32 in the energy range tested. Moreover, as illustrated in Figure 6, the material of the invention exhibited a higher COF than traditional, low density, C/BN materials. The stable COF data for the C/BN composites allows for much better predictability in designing the braking system and resolution of issues for variability in the feel of brakes to pilots. It has also been shown that the COF of boron nitride is less sensitive to the presence of water (G.W. Rowe, Wear, vol. 3, page 274, 1960). This will also help in resolving the issue of morning sickness, by decreasing the change in the COF as the brakes dry out, caused by heating, during 30 use.

7) Preparation of high density 3D C/BN composites.

The procedure previously described for the C/BN composite of Example 1 was applied on a 3D needled preform instead of the chopped carbon fibers. The
5 preform had a 28% fiber volume and a bulk density of about 0.45 g/cc. The fiber of the preform was polyacrylonitrile-derived, with an average fiber diameter of 9 microns and a density of about 1.78 g/cc. Samples of the preform were provided by the Goodrich Corporation (Brecksville, OH) or Albany International
Techniweave (Rochester, NH). The process was repeated up to three times,
10 yielding final 3D C/BN composites with a density of 1.63 g/cc to 1.72 g/cc.

8) Preparation of high density 3D C/C/BN composites.

A sample of 3D needled preform such as that used in Example 7 was carbon vapor infiltrated to increase density to ~ 1.3 g/cc, then placed in a steel
15 pressure vessel and heated under roughing vacuum for 12 hours. The pressure vessel was backfilled with dry nitrogen and borazine oligomer was added. The preform and borazine were reacted for an additional 12 hours in the steel pressure vessel. In a dry box, the borazine soaked sample was placed in a mold and an excess of borazine oligomer was added. The rest of the procedure then followed
20 the same steps as previously described for the C/BN composite of Example 1. This process was typically carried out four times, yielding a product with a density of 1.62 g/cc to 1.80 g/cc.

9) X-ray diffraction data of high density 3D C/C/BN composites.

As seen in Figure 7, X-ray diffraction scans of the high density 3D C/C/BN
25 composite material displayed a highly ordered boron nitride phase with an interlayer spacing of 3.38 Å. The more defined shoulder appearing next to the boron nitride peak is due to the vapor deposited carbon matrix that tends to order itself on the surface of the carbon fiber.

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10) Wear rate testing of high density 3D C/C/BN composites.

As seen in Figure 8 and Figure 9, the 3D C/C/BN systems displayed a wear rate so low that it is, at best, very difficult to measure accurately. The change in mass of the samples is very small, on the order of micrograms. The wear rate of the 3D C/C/BN is a full order of magnitude lower than the wear rates of 3D C/C up to an energy level of approximately 600 kJ/kg. At approximately 900 kJ/kg the wear rate of the 3D C/C/BN composites starts to increase gradually due to oxidation but only at higher interfacial pressures. In particular, the wear rate was near zero at low energy levels (<300 kJ/kg) that represent the taxiing condition of aircraft braking. This regime accounts for the majority of wear over the life of the brakes and may be significantly decreased with the 3D C/C/BN composite. For example, the Boeing 777, designed for 3000 landings per overhaul (LPO), only realizes 1500 LPO due to extra taxiing caused by airport congestion. This wear would be essentially eliminated with the use of the 3D C/C/BN material. The samples were tested at interfacial pressures of 0.25 MPa and 0.5 MPa, and the wear rate only marginally increased as the interfacial pressures was raised, as opposed to the more pronounced increases registered with 3D C/C and 3D C/BN materials.

11) Friction testing of high density 3D C/C/BN composites.

At an interfacial pressure of 0.25 MPa, the 3D C/C/BN displays a COF of approximately 0.2 (Figure 10). However, increased pressure leads to a relative decrease in the COF that is less substantial than that registered on 3D C/C and 3D C/BN materials (Figure 11). It is interesting to note that at lower interfacial pressures and high energy levels, the COF actually increases. This property would be especially important in the case of an RTO where a higher COF is needed to affect decreased stop time and distance, thus contributing to passenger safety.